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THE PHYSICAL CHEMISTRY OF DISINFECTION, I *

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Various attempts have been made to apply the principles of physical chemistry in the standardization of disinfectants. These, however, have not been wholly successful, altho their entire impracticability has not been demonstrated.

One of the simplest of physico-chemical measurements which can be used to show changes in ion-concentrations in solutions, is that of electrical conductivity. Protein degradation may be followed by such a method — the conductivity increasing as the chemical change progresses. With the aid of this principle Schryver and Lessing[1] devised a method for comparing the relative antiseptic values of disinfectants. The rate of chemical change produced in a substrate by bacterial infection was taken as a measure of the vigor of the growth, and the effect on this rate of the presence of any given disinfectant was compared to the effect produced by carbolic acid. The method was designed to measure inhibition rather than sterilization.

It has been shown by Madsen and Nyman[2] and Chick[3] that the killing of bacteria by disinfectants sometimes simulates a monomolecular reaction, in which the bacteria take the place of one of the reacting substances. The other substance, the disinfectant, is present in such excess that its concentration is not materially changed during the reaction. The process may be compared to the inversion of sugar. For example, if the temperature is constant, the reaction may be represented by the equation,

$$-\frac{db}{dt} = kb \qquad (1)$$

where "b" represents the number of bacteria present in unit volume after any time, "t," has elapsed and "k" is the velocity constant. After integration the equation has the form,

$$\log\frac{B}{b} = kt \qquad (2)$$

in which "B" is the number of bacteria initially present.

Chick,[3] in her work on the laws of disinfection, studied the various phases involved in this reaction, such as the reaction velocity of disinfection, the effect

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[1] Jour. Soc. Chem. Ind., 1909, 28, p. 60.

[2] Centralbl. f. Bakteriol., R., 1907, 40, p. 113. Ztschr. f. Hyg. u. Infektionskrankh., 1908, 57, p. 388.

[3] Jour. Hyg., 1908, 8, p. 92.

[4] Jour. Infect. Dis., 1911, 8, p. 27.

on its germicidal action of varying the concentration of a disinfectant, and the influence of temperature upon the velocity of disinfection. Using these principles of physical chemistry, Phelps[4] made the following suggestions to be applied in the standardization of disinfectants. Taking into account the effect of varying the concentration of a disinfectant, we have

$$-\frac{db}{dt} = KbC^{n} \tag{3}$$

After integration

$$\mathrm{Log}\,\frac{B}{b} = KC^{n}t \tag{4}$$

"C" is the concentration of disinfectant and "n" the exponent indicating the order of reaction. This may be determined from 2 experiments in which different values of "C" are used.

$$n = \log_{10}\frac{k'}{k'} \div \log_{10}\frac{c'}{c} \tag{5}$$

"C" and "n" being known, "K," the velocity constant in Equation 4, may be calculated. The influence of temperature may be mathematically expressed by the equation

$$\frac{K'}{K} = \theta^{(T' - T)} \tag{6}$$

in which "K'" and "K" are constants of the reaction at temperatures "T" and "T'," respectively, and θ is the temperature coefficient. This coefficient is important since the action of the disinfectant is proportional to the temperature. With the value of θ known, the velocity constant of a disinfectant at any temperature may be calculated from the equation

$$K_{T°} = K_{20°} \times \theta^{(T° - T^{20°})} \tag{7}$$

These three constants, the velocity constant "K," the concentration exponent "n," and the temperature coefficient θ, are supposed to define the three essential characteristics of any disinfectant. These three values may be obtained for a given antiseptic substance and compared with the same values obtained for carbolic acid.

While such methods as the two described may have some advantages, they certainly have at present many disadvantages. But they serve to illustrate the hope that an intensive study of the physical chemistry of disinfection may not be without practical importance. In the investigation to be described in this and following papers we have undertaken to apply physico-chemical principles and methods to what may be considered a biologic problem; that is, the mechanism of disinfection.

THE ACTION OF THE HYDROGEN ION

The first work on the relation of electrolytic dissociation to the destructive action of toxic substances was done by Dreser. Later, other investigators experimented with different metallic salts.

Bial,[5] Chick,[3] Madsen and Nyman,[2] and Reichel[6] found in the case of mercury salts that the disinfecting action was proportional to the Hg-ion content, and was decreased on the addition of sodium chlorid. Other metallic salts behaved in a similar way.

Acids show a like behavior, their antiseptic action depending, at least partly, on the degree of dissociation, and on the concentration of the hydrogen ion. For example, Bial[5] found that the less an acid was dissociated, the higher the concentration required for a given killing power toward yeast. In the presence of a salt having a common ion, a condition which gives a decrease in the hydrogen-ion concentration, this power is much diminished.

Other investigators have observed the same phenomenon. Winslow and Lockridge,[7] using B. coli and B. typhosus, found that the disinfecting power of acids was proportional to the concentration of the hydogen ion, but that organic acids have a stronger action than inorganic acids having the same hydrogen-ion concentration. That the anion has little disinfecting power has been shown by Daniels[8] in some experiments with alkali formates.

In some recent papers Paul, Birstein, and Reuss[9] put forward the view that not only does the hydrogen-ion concentration play an important rôle in the kinetics of disinfection, but that the anions and the undissociated molecules are also responsible factors; that is, they accelerate the action of the hydrogen ions. These views are supported by considerable experimental evidence, but we can hardly regard it as conclusive, particularly in view of some preliminary experiments of our own.

The first part of this investigation has therefore been undertaken in order to show, conclusively, the rôles which undissociated acids, hydrogen ions, and anions play in disinfection. For the representative acid we have chosen formic acid, because of its relatively high germicidal power and because its physico-chemical constants either are known or can be readily determined. It is also well adapted for experiments on adsorption, which form a part of this investigation.

Test Organism.—The organism used for the investigation was B. typhosus (Hopkins), obtained through the courtesy of the Hygienic Laboratory, Washington. From the stock culture agar slants were made, kept in an ice chest, and transferred about once a month. The culture actually used was made by inoculating nutrient broth (+ 1.5), and making transfers into fresh broth tubes twice again, the period between each transfer being 24 hours. The growth in the third tube was used after exactly 24 hours. In this way the resistance of the organism was kept practically constant. If more than 3 transfers into broth were made, the culture gradually lost its vitality. Table 1, which it seems worth while to insert here, will emphasize this statement.

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[5] Ztschr. f. physical. Chem., 1902, 40, p. 513.

[6] Biochem. Ztschr., 1909, 22, p. 149.

[7] Jour. Infect. Dis., 1906, 3, p. 547.

[8] Thesis, Mass. Inst. Technology, 1912.

[9] Biochem. Ztschr., 1910, 29, pp. 202, 239.

TABLE 1

THE RELATION BETWEEN AGE AND THE RESISTANCE OF BROTH CULTURES OF B. TYPHOSUS TOWARD FORMIC ACID

Dilution of HCOOH	Time in Minutes Required for Complete Killing		
	Transferred for 3 Days	Transferred for 20-25 Days	Transferred for 3 Months
1-200	25	25	5
1-300	35	45	10
1-400	50	55	12½
1-500	105	95	12½
1-600	175	130	15

Temperature.—All our experiments were performed at 20 C. This temperature was maintained in a water bath by means of an automatic electric heater and regulator, and did not vary more than 0.05° during any experiments, except those requiring long periods of time, in which the variation was slightly greater, but well within the limits of error of the work.

Medium.—The medium used was nutrient broth, made from Liebig's Extract, with a reaction of + 1.5 (phenolphthalein). In order to have the culture tubes all contain exactly the same amount of broth, a Vanier automatic 10-c.c. pipet was used for filling them. This proved an accurate, easy, and rapid method.

Method.—In all the tests recorded in this paper, the technic used was substantially that proposed by the Hygienic Laboratory for the standardization of disinfectants,[10] the time of exposure being extended, of course, to suit our needs. The broth culture of B. typhosus (Hopkins) as described above, was filtered through sterile filter paper and placed in the water bath. After it had remained there long enough to come to the required temperature, a series of seeding tubes containing 5 c.c. of various amounts of acid or acid-salt mixture were inoculated with 0.1 c.c. of the filtered culture (approximately 9,000,000 bacteria) from a 1-c.c. graduated pipet at ½-minute intervals. Subcultures into broth were then made with the standard loop (4 mm. in diameter) after the required time had elapsed. The subculture tubes were incubated at 37 C. for 48 hours and were then examined for growth. We found in all cases but one that 48 hours were sufficient for developing any surviving organisms.

EXPERIMENTAL RESULTS

The first tests were made to determine the relation of the concentration of hydrogen ion, formed by the dissociation of formic acid in water solution, to its disinfecting power. Table 2 gives the data and Chart 1 shows a curve obtained by plotting the time of exposure required for complete disinfection against the hydrogen-ion concentration. Similar curves could be obtained for the formate anion or the undissociated molecule. The disinfecting power might therefore be proportional to any one of the three.

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[10] Bull. Hyg. Lab., U. S. P. H. and M.-H. S., 1912, 82.

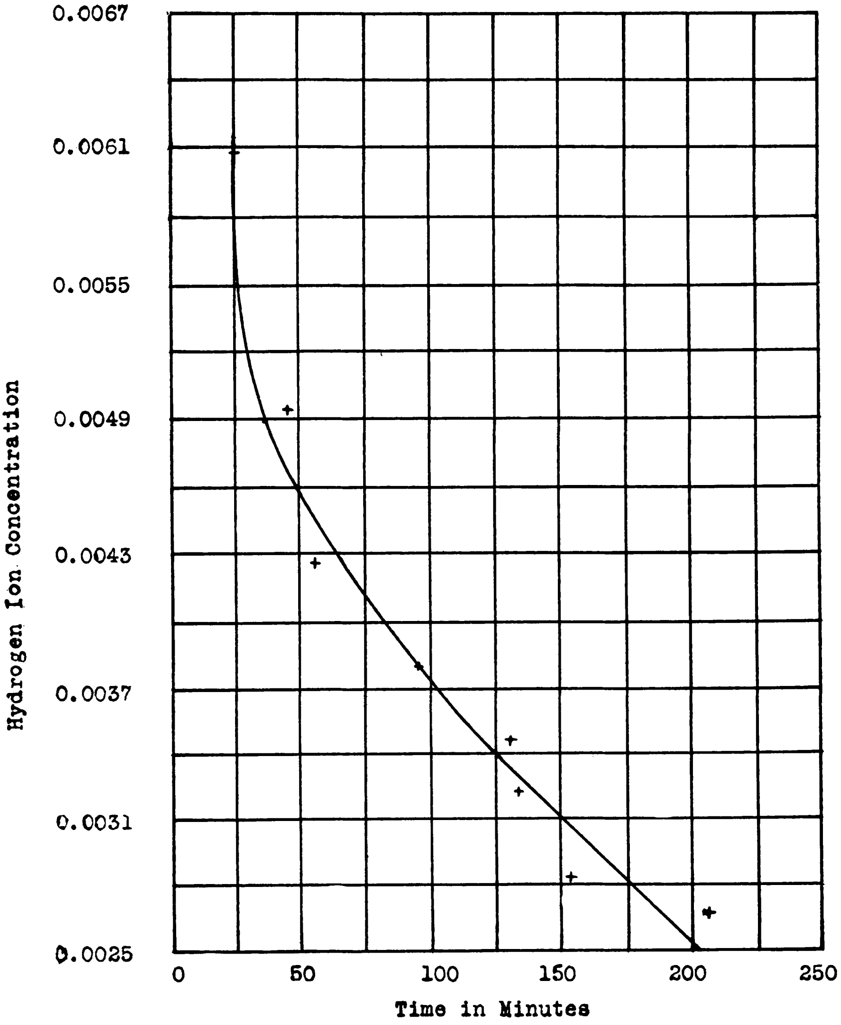

Chart 1.—The relation of the concentration of hydrogen ion, formed by the dissociation of formic acid in water solution, to its disinfecting power.

If the disinfecting action is proportional to the hydrogen-ion concentration, then by decreasing the latter in an acid solution of a given normality, the disinfecting action should be correspondingly decreased. The simplest method of changing the hydrogen-ion concentration is by adding a salt with a common anion. For this purpose ammonium formate and sodium formate were separately added to 0.0723 normal formic acid. In each experiment controls were made with pure acid and with pure salt. No appreciable disinfecting power was shown by the latter. Tables 3 and 4 show the results.

TABLE 2

Relation of Concentration of Formic Acid to Disinfection

Dilution by Volume	Normality	H^+ Ion Concentration, Mols per Liter	Time in Minutes Required for Complete Killing
1-200	.1879	.006072	25
1-300	.1253	.004944	45
1-400	.09393	.004260	55
1-500	.07514	.003796	95
1-600	.06262	.003450	130
1-700	.05367	.003210	135
1-900	.04174	.002818	155
1-1000	.03757	.002670	205

Culture transferred 20-25 days.
H^+ ion concentration calculated on basis[11] of $K_{20°} = 2.04 \times 10^{-4}$

TABLE 3

The Effect on Disinfection of the Addition of Ammonium Formate to Formic Acid

Composition of Disinfectant	Time in Hours for Complete Killing
.0723 HCOOH + 0.0 N $HCOONH_4$	2¾
.0723 HCOOH + 1.0 N $HCOONH_4$	Not complete in 8 hours
.0723 HCOOH + 0.6 N $HCOONH_4$	Not complete in 8 hours
.0723 HCOOH + 0.2 N $HCOONH_4$	Not complete in 8 hours
.0723 HCOOH + 0.08 N $HCOONH_4$	7
.0723 HCOOH + 0.04 N $HCOONH_4$	5¼
.0723 HCOOH + 0.02 N $HCOONH_4$	4
.0723 HCOOH + 0.004 N $HCOONH_4$	2½
.0723 HCOOH + 0.0015 N $HCOONH_4$	2¼
.0 N HCOOH + 2.0 N $HCOONH_4$	Not complete in 8 hours
.0 N HCOOH + 1.0 N $HCOONH_4$	Not complete in 8 hours
.0 N HCOOH + 0.08 N $HCOONH_4$	Not complete in 8 hours

Culture transferred 3 days.

TABLE 4

The Effect on Disinfection of the Addition of Sodium Formate to Formic Acid

Acid-Salt Mixture				Pure Acid	
Normality Acid	Normality Salt	H^+ Ion Concentration, Mols per Liter	Time in Minutes for Killing	H^+ Ion Concentration, Mols per Liter	Time in Minutes for Killing
.1879	.006515	.00577	10	.006072	5
.1253	.004343	.00475	15	.004944	10
.09393	.003317	.00411	15	.004260	10
.07514	.002605	.00337	20	.003796	12½
.06262	.002171	.00337	25	.003450	15

Culture transferred 2½ months.

The hydrogen-ion concentrations for the acid-salt mixtures were calculated on the assumption of complete ionization of the salt.

Ratio of HCOOH/HCOONa = 29.

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[11] H. Jahn: Ztschr. f. physical. Chem., 1895, 16, p. 85.

Tables 3 and 4 give typical data, which may be easily duplicated. They show clearly certain tendencies:

1. The addition to an acid of a salt containing an anion common to the acid greatly decreases the acid's disinfecting power, except when only very small amounts of the salt are added.

2. The decrease in disinfecting action is only approximately proportional to the change in hydrogen-ion concentration . In other words, the retarding action of the salt is greater than can be accounted for by the change in ionization produced.

3. The formate ion has, of itself, no antiseptic properties.

4. The undissociated formic acid molecule has little, if any, disinfecting action, since an increase in its concentration, obtained by adding salt to acid, did not cause increased activity of the solution.

5. The hydrogen ion is the agent responsible for disinfecting power. This, however, may be influenced by the presence of the formate ion or of undissociated formic acid molecules.

The results obtained, which show decreased disinfection in the presence of salts, are in direct contradiction to the observations of Bial,[5] who found that the addition of a neutral salt with a common ion to an acid, first decreased its antiseptic power but increased it on further additions of the salt. For example, in an acetic acid solution of 0.025 normality the antiseptic power was decreased by the addition of sodium acetate in low concentrations, but when a concentration of 1.2 normal was reached its power was greatly increased.

Our conclusion that the hydrogen ion is the responsible agent may be further tested by the use of an equation proposed by Chick.[3] She found that a logarithmic relation existed between the concentration of a disinfectant like phenol and the time taken for disinfection. That is, the expression $1/t_{n-}t_0 \log C_nt_n/C_0t_0$ remained constant in value. With silver nitrate and B. paratyphosus the equation also held, since silver nitrate in dilute solution is practically all dissociated. The same was true of mercuric chlorid, if in place of concentration of $HgCl_2$ numbers were inserted representing the concentration of mercuric ion. These facts confirm the theory that the metallic ion is the true disinfecting agent in the case of metallic salts. Hence, in our case, if the hydrogen ion is the real disinfecting agent, this same equation should give constant values when calculated on the basis of the ion concentration. Table 5 gives the values calculated with both the total concentration of the acid and that of the hydrogen ion.

TABLE 5

CONSTANTS CALCULATED FOR TOTAL ACID AND FOR HYDROGEN ION

Normality	H^+ Ion Concentration, Mols per Liter	Time in Minutes for Killing	Values of Expression $\frac{1}{C_o - C_n} \log_{10} \frac{C_n t_n}{C_o t_o}$	
				K_h
.1879	.006072	25	....	.....
.1253	.004944	45	1.27	147.3
.09393	.004260	55	0.44	104.0
.07514	.003796	95	1.61	165.1
.06262	.003450	130	1.91	179.5
.05367	.003210	135	1.40	159.2
.04174	.002818	155	1.70	141.0
.03757	.002670	205	1.43	163.8

K_n = constant calculated from normality with initial values $C_o = 0.1879$ and $t_o = 25$ min.
K_h = constant calculated from H^+ ion concentration with initial values $C_o = 0.006072$ and $t_o = 25$ min.

While these results are not absolutely definite, still the percentage deviation in K is less when the calculation is made on the basis of the hydrogen-ion concentration. This therefore aids in confirming our experimental results.

If the hydrogen ion is the true disinfecting agent, then we must account for the fact that when its concentration is decreased by adding a common-ion salt its disinfecting power is more diminished than can be accounted for by its change in concentration. Furthermore, Bial,[5] Frei and Margadant,[12] Scheurlen,[6] and Eisenberg and Okolska[13] have all demonstrated that neutral salts which themselves are not disinfectants or antiseptics have the power of improving the quality of a disinfectant to which they are added. For instance, small concentrations of salt will considerably increase the poisonous action of cresol, and a 0.1% phenol solution containing just enough sodium chlorid not to cause turbidity, is as efficient a disinfectant as a concentrated phenol solution.

Why, then, should a formate have apparently just the opposite action when added to a formic acid solution? In order to answer this and to throw more light on the real retarding agent, another series of experiments was made. If we could add a formate to a solution of formic acid in such a way that the concentrations of hydrogen ion and of undissociated formic acid would not be affected, we should be able to show the true action of the salt. This may be done by the use of the so called "Isohydric Principle."

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[12] Ztschr. f. Infektionskrankh., 1914, 15, pp. 273, 350, 407.
[13] Centralbl. f. Bakteriol., I, O., 1913, 69, p. 312.

In general, when we mix two electrolytic solutions, each dissolved substance alters the number of ions and thus affects the dissociation of the other. From the law of mass action, however, as applied to electrolytic equilibrium, we ascertain that there must be certain solutions which can be mixed together without alteration in the nature or number of ions, and therefore without affecting the conducting power, or the dissociation of either of the two dissolved substances. Such solutions are said to be isohydric. The following is the derivation, mathematically, for isohydry in the case of formic acid and ammonium formate solutions. Before mixing, let us denote the concentration of NH_4 ion by C_{NH_4}; of the formate ion of the salt, C_{Fs}; of the formate ion of the acid, C_{Fa}; of H+ion, C_H; and of the undissociated acid molecule, C_{HF}. After mixing, they are denoted respectively by C'_{NH_4}, C'_F, C'_H and C'_{HF}. "v_s" equals the volume of the salt solution before mixing and "v_a" equals the volume of the acid solution before mixing. The total volume after mixing is then $v_s + v_a$.

$$C'_H = \frac{C_H . v_a}{v_a + v_s}$$

$$C'_F = \frac{C_{Fa} . v_a}{v_a + v_s} + \frac{C_{Fs} . v_s}{v_a + v_s}$$

$$C'_{HF} = \frac{C_{HF} . v_a}{v_a + v_s}$$

The equilibrium equation for the acid before mixing is

$$\frac{(H^+)(F^-)}{(HF)} = K_1 \text{ or } \frac{C_H . C_{Fa}}{C_{HF}} = K_1$$

Its equilibrium equation after mixing will be

$$\frac{C'_H \, C'_F}{C'_{HF}} = K_2$$

After substitution of the values given

$$\frac{C_H . v_a}{v_a + v_s}\left(\frac{C_{Fa} . v_a}{v_a + v_s} + \frac{C_{Fs} . v_s}{v_a + v_s}\right) = K_2 \cdot \frac{C_{HF} . v_a}{v_a + v_s}$$

$$\text{or } \frac{C_H}{C_{HF}}\left(\frac{C_{Fa} . v_a}{v_a + v_s} + \frac{C_{Fs} . v_s}{v_a + v_s}\right) = K_2$$

In order that the ionization of the acid may not be changed on mixing, K_1 must be equal to K_2

Hence
$$\frac{C_H . C_{Fa}}{C_{HF}} = \frac{C_H}{C_{HF}}\left(\frac{C_{Fa} . v_a}{v_a + v_s} + \frac{C_{Fs} . v_s}{v_a + v_s}\right)$$

$$C_{Fa} = \frac{C_{Fa} . v_a}{v_a + v_s} + \frac{C_{Fs} . v_s}{v_a + v_s}$$

This ($K_1 = K_2$) can only be true when

$$C_{Fa} = C_{Fs}$$

For then

$$C_{Fa} = \frac{C_{Fa} . v_a}{v_a + v_s} + \frac{C_{Fa} . v_s}{v_a + v_s}$$

$$= C_{Fa}\left(\frac{v_a + v_s}{v_a + v_s}\right) = C_{Fa}$$

We may say, therefore, that solutions of electrolytes are isohydric when the concentration of the common ion in the different solutions is the same. In other words, if we make the concentrations of the anions of our solutions of formic acid and ammonium formate equal before mixing, there will be no change in the ionization of the acid after mixing. Experiments were tried with 5 such solutions to determine the effect of the salt on the disinfecting power of the acid.

The procedure for these isohydric experiments was as follows:

1. Calculate C_{F_a} in 20 c.c. of x normal formic acid solution.
2. Calculate the volume of x′ normal ammonium formate solution that contains the same concentration of anion.
3. Mix the two electrolytes.
4. Calculate C_H in the mixture.
5. (a) Take 5 c.c. of this mixture for the experiment.
   (b) Take 5 c.c. of pure acid containing the same H^+ ion concentration as in 4 and run an experiment simultaneously with (a).

The concentrations of the formate ion from the salt were obtained by using the average γ values of univalent salts taken from Noyes and Sherrill's "General Principles of Chemistry."

TABLE 6

IONIZATION OF AMMONIUM FORMATE SOLUTIONS

Concentration of $HCOO^-$ from $HCOONH_4$ Mols per Liter	Normal Concentration of Salt	Values of γ for Univalent Salts
.00096	.001	.96
.0092	.01	.92
.0180	.02	.90
.0435	.05	.87
.0840	.10	.84

TABLE 7

CONCENTRATIONS OF DIFFERENT COMPONENTS IN THE ISOHYDRIC MIXTURES

Iso-hydric Mix-ture	Volume of 0.03757 N HCOOH	Volume of 0.0095 N $HCOONH_4$	Volume of Mix-ture	Concentration in Mixture of			Normality of Acid Blanks with Same α Concentration as Mixture
				H^+ ion	NH^+_4 ion	$HCOO^-$ ion	
1	20	8	28	.00618	.00247	.00865	.194
2	20	12	32	.00541	.00324	.00865	.150
3	15	12	27	.00481	.00384	.00865	.119
4	15	15	30	.00433	.00432	.00865	.0968
5	10	14	24	.00360	.00505	.00865	.068

TABLE 8

ISOHYDRIC EXPERIMENTS I AND II WITH AMMONIUM FORMATE

	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	II	II
Minutes......	5	7½	7½	10	10	12½	15	15	20	20	25	25	30	30	35	32½	40	35	45	37½	..	40						
Mixture 1....	+	+	+	+	+	+	—	—	—	—	—	—	—	—	—	..	—											
Blank 1......	..	..	..	..	..	..	..	..	+	+	+	—	+	—	+	—	—	—	—	—	..	—						
Minutes......	7½	12½	10	15	15	17½	20	20	25	22½	30	25	35	30	40	35	45	40	50	45	55	50	60	55	..	60		
Mixture 2....	+	+	+	+	+	+	—	—	+	+	—	—	—	—	—	—	—	—	—	..	—							
Blank 2......	+	..	+	..	+	..	+	+	+	+	+	+	+	+	+	—	+	—	—	—	—	—	—	—	..	—		
Minutes......	10	12½	15	15	20	17½	25	20	30	22½	35	25	55	30	60	35	65	40	70	45	80	50	90	55	..	60	65	70
Mixture 3....	+	+	+	+	+	+	—	—	—	—	—	—	..	—	..	—												
Blank 3......	..	..	..	..	..	..	..	..	..	..	..	+	+	+	+	+	+	+	+	+	—	—	—	—	..	—	—	—
Minutes......	30	20	35	25	40	30	45	35	50	40	80	90	90	95	100	100	110	105	120	110	130	115	140	120	150	125	130	135
Mixture 4....	+	+	+	—	—	—	—	—	—	—																		
Blank 4......	..	..	..	..	..	..	..	..	..	..	+	+	+	+	+	+	—	—	+	+	—	—	—	—	—	—	—	—
Minutes......	100	35	110	40	120	45	160	50	170	55	180	60	190	150	200	160	210	170	...	175	...	180	...	185	...	190	195	200
Mixture 5....	—	+	—	—	—	—	..	—	..	—	..	—																
Blank 5......	..	..	..	..	..	..	+	..	+	..	+	..	—	+	—	+	—	+	..	—	..	—	..	—	..	—	—	—

The time in minutes gives the exposure of 0.1 c.c. of broth culture of B. typhosus (Hopkins). The sign + signifies growth; — signifies complete killing.

Culture transferred 3 days.

TABLE 9

ISOHYDRIC EXPERIMENT 3 WITH SODIUM FORMATE

Minutes	5	7½	10	15	20	25	30	35	40	45						
Mixture 1	+	+	+	—	—	—	—									
Blank 1	..	..	..	..	+	—	—	—	—	—						
Minutes	7½	10	15	20	25	30	35	40	45							
Mixture 2	+	+	—	—	—	—										
Blank 2	..	..	..	+	+	—	—	—	—							
Minutes	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	
Mixture 3	+	—	+	+	—	—										
Blank 3	..	..	..	..	+	—	+	—	+	+	+	+	+	—	—	
Minutes	10	15	20	25	30	35	40	100	105	110	115	120	125	130	135	135
Mixture 4	+	+	—	—	—	—	—									
Blank 4	..	..	..	..	..	..	..	+	+	+	—	—	—	—	—	
Minutes	35	40	45	50	55	60	65	70	75	150	155	160	165	170	175	180
Mixture 5	+	+	+	+	—	—	—	—	—							
Blank 5	..	..	..	..	..	..	..	..	..	+	+	+	—	+	—	—

See notes with Table 8.

Tables 8 and 9 show the increase in disinfecting power caused by the addition of formates to formic acid. As no change was made in the concentration of the hydrogen ion or of the undissociated formic acid molecule, the increase can be attributed only to the presence of increased amounts of the formate ions. Since these have been shown to have no direct disinfecting action, they must therefore act as accelerating or catalyzing agents. The retarding effect noted in Tables 3 and 4 must therefore be due to the decrease in hydrogen-ion concenration and probably also to a negative catalytic action of the undissociated formic acid. In any acid solution the presence of anions, formed by dissociation of the acid, will cause an acceleration in the disinfecting action, dependent on the nature of the anions, and there will also be a retarding effect due to the presence of the undissociated molecules. The apparent antiseptic power of the acid will be a combination of the power of the hydrogen ion with these two influences.

As a large amount of work has been done on the action of salts as accelerators in disinfection, it is advisable to discuss the results recorded in the three last tables in the light of results obtained where there is no common-ion effect.

THE ACTION OF SALTS

For our purposes, salts may be divided into 2 classes—those which are themselves disinfectants, such as silver nitrate and mercuric chlorid; and those which have no such properties, such as sodium chlorid, sodium nitrate, etc. For those of the first class the disinfecting action has been shown to be proportional to the concentration of the cation.[4] This is analogous to the case of acids, which we have discussed. The second class is of particular interest in a study of disinfection.

Bial[5] in 1902 observed that the addition of a salt, with a common ion, to an acid influenced its antiseptic power. Frei and Margadant[12] found that salts in small quantities greatly influenced the disinfecting action of cresol, but that the effect was not proportional to the concentration of the salt, and that the action of the salt and cresol was not additive. They also suggested that the ions from the salts influenced the disinfectant in opposite directions, the final effect being the resultant of the two actions. Scheurlen[6] found that sodium chlorid increased the efficiency of phenol. Eisenberg and Okolska[13] showed that lipoid-soluble antiseptics were greatly improved by the addition of neutral salt solutions. In almost all cases investigated, neutral salts were found to increase disinfecting properties. Exceptions were noted in the cases[13] of mercuric chlorid, urea, and potassium permanganate, in which addition of salt retarded the action. Alkaline salts, such as K_2HPO_4, $KAsO_2$, etc., acted more energetically than did neutral salts.

That some relation exists between the concentration of an added salt and its accelerating effect, is quite evident. Reichel[6] and Paul, Birstein, and Reuss[9] have made experiments and suggestions along this line. The last named suggested the equation

$$K_2 = K_1An$$

in which "A" is the accelerating factor of the salt, "n" its concentration, and "K_1" and "K_2" the disinfection-velocity constants of the acid and of the acid-salt mixture, respectively. The relation

$$K_2 = K_1 (1 - An)$$

has also been suggested, in which "A" is a proportionality factor.

The action of the various anions and cations has also been studied by Frei and Margadant,[12] who arranged each in a series showing the extent of its influence. In general, the anions have a much stronger action than have the cations. The latter sometimes retard the disinfecting action.

In order to know definitely whether or not salts other than formates have the same influence on the disinfecting power of formic acid as on other disinfectants, tests were made with sodium chlorid and sodium nitrate. The results are recorded in Tables 10 and 11.

These results confirm those of other investigators. We wish to point out particularly the very great effect produced by very small amounts of salt. The influence on the disinfecting power of formic acid is essentially of the same order as that of sodium formate and ammonium formate in isohydric mixtures. The salts by themselves show no appreciable antiseptic action. A series of experiments was also made with higher concentrations of sodium nitrate—0.484, 0.601, 0.683, 0.742 and 0.819 normal, respectively—and the same acid concentrations as shown in the tables, but the action was so rapid that the time of killing could not be determined.

TABLE 10

THE INFLUENCE OF A NEUTRAL SALT ON THE DISINFECTING POWER OF AN ACID

Formic Acid and Sodium Nitrate

Minutes.....	5	10	15	20	25	30	35						
Mixture 1...	+	—	—	—									
Blank 1.....	..	+	+	—	—	+	—						
Minutes.....	7½	10	15	20	25	30	35	40					
Mixture 2...	+	+	—	—	—								
Blank 2.....	..	..	+	+	—	—	—	—					
Minutes.....	10	15	20	25	30	35	50	55	60	65	70	75	80
Mixture 3...	+	+	+	—	+	—							
Blank 3.....	..	..	..	..	..	..	+	+	—	—	—	—	—
Minutes.....	10	15	20	25	30	35	40	100	105	110	115		
Mixture 4...	+	+	—	+	—	—	—						
Blank 4.....	..	..	..	..	..	..	..	—	—	—	—		
Minutes.....	20	25	30	35	40	45	155	160	165	170			
Mixture 5...	+	+	+	—	—	—							
Blank 5.....	..	..	..	..	..	..	+	—	—	—			

The salt concentrations in the mixtures are, respectively, 0.00271, 0.003563, 0.00422, 0.00475, 0.00554 normal.

The acid concentrations, designated as blanks, are the same as those of the isohydric mixtures (See Table 7).

TABLE 11

THE INFLUENCE OF A NEUTRAL SALT ON THE DISINFECTING POWER OF AN ACID

Formic Acid and Sodium Chlorid

Minutes.....	10	15	20	25	30	35							
Mixture 1...	+	+	+	—									
Blank 1.....	+	+	+	—	—	—							
Minutes.....	7½	10	15	20	25	30	35	40					
Mixture 2...	+	+	+	—	—								
Blank 2.....	..	..	+	+	+	+	+	—					
Minutes.....	7½	10	15	20	25	30	35	65	70	75	80		
Mixture 3...	+	+	+	—	—	—	—						
Blank 3.....	..	..	..	..	..	..	..	+	+	+	—		
Minutes.....	20	25	30	35	40	45	100	105	110	115	120	125	
Mixture 4...	+	+	+	+	—	—							
Blank 4.....	..	..	..	..	..	..	+	+	+	—	+	—	
Minutes.....	50	55	60	65	70	75	140	145	150	155	160	165	170
Mixture 5...	+	+	+	—	+	—							
Blank 5.....	..	..	..	..	..	..	+	+	+	—	—	+	—

See notes with Table 10.

SUMMARY

Acids act as disinfectants through the agency of the hydrogen ions produced by electrolytic dissociation.

The disinfecting power of an acid is approximately proportional to the hydrogen-ion concentration.

The addition to an acid of a salt containing an anion common to this acid, diminishes its disinfecting power, as the result of a decrease in the hydrogen-ion concentration and an increase in the concentration of the undissociated acid molecules.

Salts which do not appreciably affect the dissociation of an acid, greatly increase the disinfecting properties of the acid.

Acid anions are positive catalyzers and undissociated acid molecules are negative catalyzers in acid disinfection.

A discussion of the mechanism of the salt effect is so closely connected with that of the mechanism of disinfection that it will be left for a subsequent article, based on work already completed in this laboratory and on investigations at present under way, involving an intensive application of physical chemistry to the problem of disinfection.